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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| (21) International Application Number: PCT/FI92/00217 (22) International Filing Date: 16 July 1992 (16.07.92) (30) Priority data: 913438 16 July 1991 (16.07.91) FI (71) Applicant (for all designated States except US): NESTE OY [FI/FI]; Keilaniemi, SF-02150 Espoo (FI). (72) Inventors; and (75) Inventors/Applicants (for US only): KNUUTTILA, Hilka [FI/FI]; Torpparintie 4, SF-06400 Porvoo (FI). LA-KOMAA, Eeva-Liisa [FI/FI]; Soukanahde 7 F 116, SF-02360 Espoo (FI). HOKKANEN, Harri [FI/FI]; Klauettitie 1 A 28, SF-00420 Helsinki (FI). | | (74) Agent: SEPPO LAINE KY; Lönnrotinkatu 19 A, SF-00120 Helsinki (FI). (81) Designated States: FI, JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, MC, NL, SE). Published With international search report. |
| (54) Title: PROCESS FOR PREPARING A POLYMERIZATION CATALYST BY VAPOURIZING CHROMIUM ACETYLACETONATE (57) Abstract The present invention concerns a process for preparing a polymerization catalyst of olefins, said catalyst containing an active chromium compound on an inorganic support. The catalyst in accordance with the invention is prepared by vapourizing chromium acetylacetonate and allowing the reagent vapours to react with the surface of, e.g., silica gel support material at 180 to 200 °C. Selective bonding of the chromium reagent to the support material is achieved by keeping the vapour pressure sufficiently high and the duration of interaction with the support sufficiently long so as to maintain an excess of the chromium compound in relation to the unnumber of available binding sites on the support material. | | |

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Process for preparing a polymerization catalyst by vapourizing chromium acetylacetonate.

The present invention relates to a process for preparing polymerization catalyst of olefins in accordance with the preamble of claim 1.

A catalyst prepared according to the invention contains a catalytically active chromium compound bonded to an inorganic support material. The preparation comprises vaporizing a suitable chromium compound and reacting the reagent vapours with an inorganic support at a temperature above the condensation temperature of the chromium compound.

The conventional Phillips-type polymerization catalyst, invented at the beginning of the 1950's, contains chromium(VI)oxide adsorbed on a silica gel support. A prior art method for the preparation of such chromium-containing catalysts includes the impregnation of an inorganic support with a chromium compound, typically an aqueous solution of chromium trioxide, followed by calcination of the support by heating in an oxidizing atmosphere at an elevated temperature (400 °C or higher). Finally, the catalyst is activated by reduction with hydrogen, carbon monoxide or ethene, whereby unsaturated chromium compounds, which are active during polymerization, are formed on the support material surface.

A drawback of the conventional preparation method of catalysts is the need for several different phases of preparation. The preparation of the catalyst is extremely sensitive to processing conditions and thus requires strict control.

Another drawback is associated with the use of solvents. Namely, the solvents used in preparation often are capable of affecting the support material thus causing changes in its surface structure.

In addition to the above-mentioned drawbacks, impurities are contained in solvents used in the preparation that can adversely affect the performance of the catalyst.

5 Further, in connection with the above-described preparation methods of heterogeneous catalysts it is difficult to control the adsorption of catalytically active materials onto the support material surface, particularly when the surface of particle in the powdered support material used is
10 structurally nonhomogeneous.

Due to these factors, the prior art methods are not easily applicable to a controlled adsorption of a metal or metal compound.

15 Moreover, in the prior art methods, the dispersion of catalytically active materials on the support material may be poor.

20 Also known in the art are methods for preparing chromium containing heterogeneous catalysts by adsorbing chromium onto the surface of an inorganic support from the vapour phase.

25 Thus, US Patent Specification No. 4,362,654 teaches a method for depositing metallic chromium in a vacuum evaporator onto a silica surface. The catalyst obtained is subsequently activated by heating in an oxidizing atmosphere at a temperature in the range from 300 to 1000 °C to achieve an
30 activated polymerization catalyst.

The above-described method has several drawbacks. For instance, metal is not selectively bonded to the support but instead, the chromium is deposited by condensation onto the
35 support material particles. Chromium adsorption on bonding sites available in the pores is not controllable, because the actual chemical bond between the chromium metal and the support is obtained only by postactivation. The regulation

of the catalyst chromium content is not easily achieved, since a major part of the evaporated metal is condensed onto the walls of the reaction vessel. Therefore, the method fails to solve the above-mentioned problems.

5

Described in the US Patent Specification No. 4,439,543 and in the paper by McDaniel, M.P., Journal of Catalysis, 76 (1982), pp. 17 - 28, is a method based on the injection of a known quantity, 0.5 - 4 ml, of chromyl chloride solution as such or diluted with carbon tetrachloride into a gas stream, and further, routing the stream onto a silica gel support. The silica gel is heated in oxidizing conditions at 400 - 1000 °C in order to remove a portion of the hydroxyl groups. The injected chromyl halide is reacted with silica so as to deposit both chromium and halogen onto the catalyst. Finally, the chromium is subjected to reduction by carbon monoxide, which was found to improve the catalyst activity.

20

The present invention is based on the concept of introducing the precursor of the catalytically active metal in vapour phase in an equal, or preferably, in excess amount in relation to the number of available binding sites on the support material surface. The support temperature is maintained above the condensation temperature of the vapour and simultaneously sufficiently high so as to attain the thermal activation energy necessary for generation of chemical bonds between the catalytically active material or its compound and the support material.

30

A method of the foregoing type is described in the Finnish Patent Specification No. 84608. This kind of a method differs from the prior art methods in several respects. The chemical bonds are formed between the metal or metal compound and the support, while no physically adsorbed metal or metal compound exists on the support material surface during the process. This goal is achieved by selecting so high a reaction temperature that no metal or metal compound exists in liquid or solid state. The invention also differs

35

from the prior art since the formation of the surface bond is determined by the content or the number of surface sites available to the catalytically active component or its precursor in the gas phase. The metal compound is used in at least an equal amount and, preferably, in excess of the available binding sites on the support material surface, contrastingly to the metering of a certain amount of chromium compound as necessary in the US Patent No. 4,439,543 and the impregnation methods. A third essential difference from conventional technology is that the method in accordance with the present invention makes it possible advantageously to prepare catalysts in which two or more catalytically active components are bonded from vapour phase onto the support material surface. Even the adsorption order of the components can be interchanged.

The FI Patent Specification No. 84608 discloses the use of chromyl chloride as a chromium containing reagent. Surprisingly, it has now been found that particularly good results are obtained when, instead of chromyl chloride, chromium acetylacetonate is employed as a volatile reagent. In the following, the abbreviation $\text{Cr}(\text{acac})_3$ will be used for the said compound.

More specifically, the process in accordance with the invention is mainly characterized by what is stated in the characterizing part of claim 1.

Interestingly, it has been discovered that by bonding the catalytically active compound in the above-described manner onto the support, a heterogeneous catalyst can be achieved whose activity at even very low contents of catalytic metal is as high as the activity of such a catalyst of multiple content of catalytically active metal that has been prepared by way of conventional methods. Compared to catalysts prepared by using chromium chloride as a volatile reagent, $\text{Cr}(\text{acac})_3$ will provide polymerization catalysts having higher activities.

According to the invention, all reagents necessary for bonding the metal compound or its precursor are reacted in the reaction chamber in gaseous state, typically only one at a time. The vapour pressure of the evaporated $\text{Cr}(\text{acac})_3$ is here maintained sufficiently high and the duration of interaction with the surface of the support material sufficiently long so as to provide the compound in at least equal, preferably in excess amount in relation to the number of binding sites available on the support material surface. Naturally, the actual number of binding sites available on the support material surface itself is a crucial factor. This parameter can be modified by heat pretreatment methods.

The reaction temperature must not drop below the temperature necessary for evaporation of the compound in order to avoid condensation or sublimation of the compound. Further, the condensation of the compound on its way to the reaction space is prevented by keeping the feed piping temperature at least at the reaction temperature.

The temperature used is selected so as to avoid decomposition of $\text{Cr}(\text{acac})_3$ and subsequent condensation of the decomposition products.

Using experimental methods, it is possible to determine a temperature range, or temperature span, in which the reaction is advantageously carried out. The lower limit of such a temperature span is determined by the condensation temperature of the $\text{Cr}(\text{acac})_3$ at the applied pressure and by the activation energy necessary for establishing the desired surface bond. Obviously, the condensation temperature of the compound is not applicable as the lower temperature limit if the condensation temperature does not impart the reagent a sufficient energy to exceed the activation energy. The upper limit is determined by the temperature at which the compound chemisorbed on the support starts to show an essential rate of desorption, that is, when the equilibrium of the chemisorption-desorption reaction has shifted toward

desorption. Since the activation and desorption energies are not generally known, the appropriate temperature must be experimentally determined.

5 When chromium acetylacetonate is used as the reagent and silica (silicon dioxide) as the support material, it is preferred to operate the method at a temperature in the range from 160 to 300 °C. According to a preferred embodiment, the temperature is kept at 180 to 280 °C.

10 The pretreatment to be described below is carried out at a temperature in the range from 200 to 900 °C. According to a preferred embodiment the pretreatment is performed at a higher temperature than the actual reaction, typically at about 400 to 900, whereas the reaction is conducted at 180 to

15 200 °C.

Since, according to the invention, the number of binding sites affects the amount of active metal bonded to the support, pretreatment and/or intermediate treatment of the

20 support is an essential factor. The pretreatment can be accomplished before the support material is loaded into the reaction vessel, or alternatively, in the reaction vessel itself prior to introducing the vapour of Cr(acac)₃ into the reaction space.

25 The number of available binding sites can be affected by, e.g., a heat treatment which controls, among other factors, the number of hydroxyl groups on the support material surface, or alternatively, by chemical processing, for

30 instance, a treatment with water vapour which increases the number of hydroxyl groups. These treatments which modify the support material can be carried out when desired during any process step prior to the removal of the catalyst from the reaction space. It is also possible to combine said

35 treatments, for instance, by treating the support material with water or water vapour after a heat treatment in order to introduce new hydroxyl groups on its surface.

The preheating can be performed by conventional means, one of which is heating in an air stream at, e.g., 200 to 900 °C.

- 5 The number of binding sites for $\text{Cr}(\text{acac})_3$ can also be reduced by using a blocking agent which binds to isolated hydroxyl groups. Thus, for instance, hexamethyl disilazane (HMDS) may be used as a blocking agent. In the case of HMDS, it is preferred to operate the process in an inert atmosphere.
- 10 According to a preferred embodiment, the HMDS treatment is carried out after preheating of the support.

- 15 The proportion of excess active material in relation to the concentration necessary to achieve a full saturation of all available binding sites on the support material surface (customarily called a monolayer coverage) is typically 1.5 to 1000-fold, preferably 2- to 100-fold. The amount of chromium acetylacetonate necessary for a monolayer coverage can be calculated from the area of the support material
- 20 determined with the help of, e.g., the BET method, and from the known molecular structure of the support material surface.

- 25 According to the method in accordance with the invention, the reaction between the vapour of $\text{Cr}(\text{acac})_3$ and the support can be carried out in air, in an inert gas atmosphere or, alternatively, under reduced pressure using advantageously an inert gas atmosphere of 1 to 10 mbar pressure. Equally, the optional pre- and posttreatment steps can be performed
- 30 in the same conditions as the actual reaction. A benefit to be gained from the use of a partial vacuum is that the reaction space is kept cleaner and the diffusion rate is increased. The reaction time is principally affected by the diffusion of vapour molecules into the support material
- 35 pores. The diffusion of the vapour molecules between the support material particles is very rapid in comparison with their diffusion into the pores. Therefore, the reaction time must be sufficiently long to allow the vapour containing the

metal or metal compound to reach adequate interaction with the binding sites of the support. In the tests performed, a reaction time of 1 to 4 h proved sufficient for the purpose.

5 The evaporated reagent can be brought to the reaction space as such, or alternatively, using an inert carrier gas such as nitrogen or noble gases.

10 In the catalyst according to the invention, the support materials advantageously used are inorganic oxides such as silicon oxide (silica), aluminium oxide, thorium oxide, zirconium oxide, magnesium oxide, titanium oxide, or mixtures thereof.

15 The catalysts in accordance with the invention can be catalysts containing chromium alone, or alternatively, catalysts containing aluminium compounds in addition to the chromium. The chromium and aluminium compounds can be introduced in a free order. Thus, the aluminium compounds,
20 such as aluminium trichloride, can be introduced before or after the bonding of $\text{Cr}(\text{acac})_3$.

The excess of the chromium acetylacetonate used in each reaction step is removed, still in gas phase, before the
25 next step by, e.g., flushing the reaction space with an inert gas. As mentioned above, it is essential that condensation of the reagent be avoided at all times during the process.

30 After bonding of the active metal compound, the ligands of the bonded chromium compounds are removed, e.g., by heat treatment. In most cases, no separate heat treatment will be needed, but the ligands are removed in connection with a typical activation operation, which comprises heating the
35 catalyst in an oxidizing atmosphere at 400 to 1000 °C. Preferably, the activation is carried out in the same reaction vessel as the reaction, while it is also possible to perform the activation in a separate reaction vessel

later at any instant prior to polymerization. The oxidizing conditions can be attained with the help of an oxygen-containing gas such as air.

- 5 In the following, the invention will be examined in more detail with the help of working examples.

Example 1A

- 10 Silica support material (EP 10, Crosfield Catalysts) was loaded in an amount of 5 to 8 g into a reaction vessel after preheating in air for 16 h at different temperatures. Physisorbed water, if any, was removed by heating in an inert atmosphere (nitrogen flow) in a fixed support bed at a
15 pressure in the range from 50 to 120 mbar chromium acetylacetonate was vaporized at 180 to 200 °C and conducted to the reaction vessel during 1 to 3 h in nitrogen flow. The reaction vessel was kept at a temperature of 200 °C during the bonding of Cr. After the reaction, the support bed was
20 purged with nitrogen for 1 to 2 hours to remove any unreacted reagent.

- The samples thus prepared were further calcinated at atmospheric pressure in a fluidized bed in air or
25 nitrogen/air atmosphere at different temperatures.

- The obtained catalysts were used for ethene polymerization at 105 °C temperature and a total pressure of 4000 kPa in an autoclave of 3 liter volume. The hydrocarbon diluent in the
30 polymerization process was isobutane. Table 1A presents the processing conditions of the catalyst and the polymerization results.

Table 1A. Properties of catalysts prepared according to the invention and polymerization results

| Sample | Preheating T/°C | Activation T/°C | Cr wt-% | Cr(VI) wt-% | PE g/g*h | MIR ₂₁ |
|--------|--------------------|--------------------|------------|----------------|-------------|-------------------|
| A | 200 | 845 | 2.3 | 1.1 | 3100 | 24.3 |
| B | 560 | 855 | 1.1 | 0.9 | 5000 | 24.8 |
| C | 580 | 880 | 1.0 | 0.8 | 5500 | 26.2 |
| D | 780 | 820 | 0.6 | 0.5 | 3100 | 20.6 |
| E | 820 | 835 | 0.7 | 0.5 | 4700 | 16.2 |

MIR₂₁ = high load melt index

Activity calculated as polyethene/g catalyst*h

Example 1B (reference)

Polymeration catalysts containing chromium were prepared as explained in example 1 of FI Patent Specification No. 84608.

The obtained catalysts were used for ethene polymerization as explained in example 1A. The catalyst characteristics and polymerization results are shown in table 1B below.

Table 1B. The activities of catalysts prepared according to the prior art

| Catalyst | Cr [%] | Cl [%] | Yield [g] | Activity [gPE/gcat*h] | MIR ₂₁ |
|----------|-----------|-----------|--------------|--------------------------|-------------------|
| F | 1.4 | 0.32 | 140 | 700 | 1.0 |
| G | 1.5 | | 220 | 1220 | 10.9 |
| H | 0.01 | <0.01 | 100 | 200 | 8.3 |

Example 2

The number of binding sites for the Cr compound was reduced by using a blocking agent known to bind to isolated hydroxyl groups. Thus, Cr acetylacetonate was bonded to silica EP 10 preheated at 200 °C and treated with the blocking reagent HMDS (hexamethyl disilazane) at 175 °C. The Cr/silica sample was calcinated in the same reaction vessel at a pressure in the range from 80 to 130 mbar with dry synthetic air in a fixed bed.

Table 2 shows the processing parameters of the catalyst, Cr concentration and polymerization results.

Table 2. Processing parameters of the catalysts

| Sample | Preheating T/°C | Activation T/°C | Cr wt-% | Cr(VI) wt-% | PE g/g*h | MIR ₂₁ |
|--------|--------------------|--------------------|------------|----------------|-------------|-------------------|
| I | 200 | 650 | 0.7 | 0.6 | 3100 | 3.8 |

Example 3

Catalysts were prepared as in Example 1A except that the activation or calcination of the catalysts was carried out in the same reaction vessel and not in a separate fluidized bed as in Example 1A.

The obtained catalysts were for ethene polymerization as described in Example 1A.

Tables 3A and 3B below present the processing conditions of the catalysts and the polymerization results. Table 3A illustrates the effect of Cr(acac)₃ reaction temperature on the properties of the catalysts. The samples were pre-calcined at 560 °C and oxidation was carried out at 400 °C.

Table 3A. Effect of Cr(acac)₃ reaction temperature on the properties of the catalysts

| Sample | J | K | L | M |
|-----------------------------------|--------|------|--------|--------|
| Cr(acac) ₃ reaction/°C | 200 | 240 | 260 | 280 |
| Cr _{tot} /wt-% | 1.51 | 1.79 | 1.95 | 2.25 |
| Cr ⁶⁺ /wt-% | 1.50 | 1.79 | 1.82 | 2.02 |
| Activity: | | | | |
| g PE/gcath | 3000 | 1900 | 2600 | 1400 |
| kg PE/gCrh | 196 | 102 | 132 | 62 |
| kg PE/gCr ⁶⁺ h | 197 | 102 | 141 | 69 |
| MI _{21.6} | 15.2 | 6.6 | 12.5 | 15.6 |
| FRR _{21.5} | 16.1 | 17.9 | 15.8 | 17.8 |
| M _w | 188500 | - | 227000 | 217500 |
| M _n | 18250 | - | 17450 | 15850 |
| D | 10.3 | - | 13.1 | 13.8 |

MI = melt index

FRR = flow rate ratio

Table 3B illustrates the effect of the silica precalcination (pretreatment) temperature on the properties of the catalysts. The reactions between the supports and the chromium reagents were carried out at 200 °C.

Table 3B. Effect of silica precalcination temperature

| Sample | N | J | O | P | Q | R |
|-----------------------------|------|--------|------|--------|------|--------|
| 5 Silica pre-calcination/°C | 200 | 560 | 560 | 650 | 820 | 820 |
| Oxidation/°C | 400 | 400 | 650 | 400 | 400 | 600 |
| Cr _{tot} /wt-% | 2.42 | 1.51 | 1.33 | 1.20 | 0.72 | 0.98 |
| Cr ⁶⁺ /wt-% | 2.34 | 1.50 | 0.70 | 1.19 | 0.62 | 0.17 |
| 10 Activity: | | | | | | |
| g PE/gcath | 700 | 3000 | 3700 | 3000 | 2400 | 1300 |
| kg PE/gCrh | 30 | 196 | 282 | 252 | 337 | 131 |
| kg PE/gCr ⁶⁺ h | 31 | 197 | 535 | 254 | 391 | 755 |
| MFR _{21.6} | 2.9 | 15.2 | 8.8 | 21.7 | 27.6 | 15.7 |
| 15 FRR _{21.5} | 24.8 | 16.1 | 18.2 | 16.4 | 16.4 | 14.9 |
| M _w | - | 188500 | - | 173500 | - | 184000 |
| M _n | - | 18250 | - | 17300 | - | 20750 |
| D | - | 10.3 | - | 10.0 | - | 8.9 |
| 20 MFR = melt flow ratio | | | | | | |

The results in Tables 3A and 3B show that when using relatively mild activation conditions it is possible to affect the product properties by changing the pretreatment temperature.

WHAT IS CLAIMED IS:

1. Process for preparing a polymerization catalyst for
olefins, said catalyst containing at least one catalytically
active chromium compound bonded to an inorganic support,
characterized in that the catalyst is prepared
by

- optionally subjecting the support material to a
pretreatment in order to modify the number of bonding
sites available on the support, said pretreatment
comprising heating said support at a temperature in
the range from 200 to 900 °C, or chemically processing
said support;
- vapourizing chromium acetylacetonate,
- routing the obtained vapour into a reaction space
wherein the vapour is reacted with the support
material at about 160 to 300 °C;
- maintaining the vapour pressure of the chromium
acetylacetonate sufficiently high and the duration of
interaction sufficiently long so as to provide at
least an equal amount of chromium acetylacetonate as
there are available bonding sites on the support
material;
- removing unreacted chromium acetylacetonate in the gas
phase from said reaction space, and
- optionally posttreating the heterogeneous chromium
containing catalyst in order to increase modify its
catalytic activity.

2. The process according to claim 1, wherein the reaction
is carried out at approx. 180 to 280 °C.

3. The process according to claim 1, wherein the
pretreatment is carried out at a temperature higher than the
reaction temperature.

4. The process according to claim 1, wherein the pretreatment is carried out at a temperature above approx. 400 °C and the actual reaction at a temperature in the range from about 180 to 200 °C.

5

5. The process according to claim 1, wherein chromium acetylacetonate is used in the reaction by excess amounts of approx. 2- to 100-fold in relation to the number of bonding sites available on the support material surface.

10

6. The process according to claim 1, wherein said support material is treated with water vapour after pretreatment with heat.

15

7. The process according to claim 1, wherein said support material is reacted with an evaporated aluminium compound after said optional pretreatment.

20

8. The process according to claim 1, wherein said chromium containing catalyst is reacted with an evaporated aluminium compound after said reaction between chromium acetylacetonate and said support material.

25

9. The process according to claim 1, wherein a part of the bonding sites of said support is blocked with a blocking agent before reacting chromium acetylacetonate with said support.

30

10. The process according to claim 9, wherein said blocking agent used is hexamethyl disilazane.

35

11. The process according to claim 9, wherein said bonding sites as blocked after said optional pretreatment of said support.

12. The process according to claim 1, wherein said catalyst is posttreated by heating in air at 400 to 1000 °C.

13. The process according to claim 1, wherein said pretreatment and the actual reaction steps are carried out under reduced pressure.

5 14. The process according to claim 1, wherein said reduced pressure is from 0.1 to 100 mbar.

10 15. The process according to claim 1, wherein said support material is selected from the group consisting of silica gel, aluminium oxide, thorium oxide, zirconium oxide, magnesium oxide, titanium oxide and mixtures thereof.

16. A polymerization catalyst for olefins prepared by a process according to any of claims 1 to 15.

INTERNATIONAL SEARCH REPORT

International Application No **PCT/FI 92/00217**

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|--|--|-------------------------------------|-----------------------|------------------------|-------------|---------------|
| I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 08 F 4/78 | | | | | | |
| II. FIELDS SEARCHED <div style="text-align: right; margin-right: 100px;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 30%; border: none;">Classification System</td> <td style="border: none;">Classification Symbols</td> </tr> <tr> <td style="border: none; height: 40px; vertical-align: bottom;">IPC5</td> <td style="border: none; vertical-align: bottom;">C 08 F</td> </tr> </table> <div style="text-align: center; margin-top: 10px;">Documentation Searched other than Minimum Documentation to the extent that such Documents are included in Fields Searched⁸</div> | | | Classification System | Classification Symbols | IPC5 | C 08 F |
| Classification System | Classification Symbols | | | | | |
| IPC5 | C 08 F | | | | | |
| SE,DK,FI,NO classes as above | | | | | | |
| III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ | | | | | | |
| Category * | Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹² | Relevant to Claim No. ¹³ | | | | |
| X | US, A, 4184979 (WILLIAM KIRCH ET AL.) 22 January 1980, see column 1, lines 6-24; column 2, lines 25-28 example 1 <div style="text-align: center;">--</div> | 1 | | | | |
| X | US, A, 4147849 (JOSEPH LIU ET AL.) 3 April 1979, see the abstract; column 2, line 13 - column 4, lines 7-9, lines 13-14 <div style="text-align: center;">--</div> | 1 | | | | |
| A | US, A, 4362654 (FRED L. VANCE, JR. ET AL.) 7 December 1982, see the abstract; column 1, lines 60-68 <div style="text-align: center;">--</div> | 1-16 | | | | |
| P,A | EP, A2, 0438132 (NESTE OY) 24 July 1991, see the abstract <div style="text-align: center;">--</div> <div style="text-align: center;">-----</div> | 1-14 | | | | |
| <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents:¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div> | | | | | | |
| IV. CERTIFICATION | | | | | | |
| Date of the Actual Completion of the International Search 14th October 1992 | Date of Mailing of this International Search Report <div style="text-align: center; font-size: 1.2em;">21 -10- 1992</div> | | | | | |
| International Searching Authority <div style="text-align: center; font-weight: bold;">SWEDISH PATENT OFFICE</div> | Signature of Authorized Officer <div style="text-align: center;"> Agneta Österman Wallin </div> | | | | | |

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.PCT/FI 92/00217**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the Swedish Patent Office EDP file on **30/09/92**
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| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|--|--|
| US-A- 4184979 | 80-01-22 | NONE | |
| US-A- 4147849 | 79-04-03 | BE-A- 859545 DE-A-C- 2709535 FR-A-B- 2342996 GB-A- 1530103 US-A- 4053437 | 78-02-01 77-09-08 77-09-30 78-10-25 77-10-11 |
| US-A- 4362654 | 82-12-07 | NONE | |
| EP-A2- 0438132 | 91-07-24 | NONE | |